

HIGH PRESSURE COSMOCHEMISTRY OF MAJOR PLANETARY INTERIORS: LABORATORY STUDIES OF THE WATER-RICH REGION OF THE SYSTEM AMMONIA-WATER

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Models of the major planets and their satellites make simple, rather arbitrary assumptions concerning deep interiors. "Rock" cores or "ice" (water-ammonia-methane) layers are often invoked without considering thermodynamic consistency. The behavior of "gas-ice" mixtures at very high pressures, however, is poorly understood. When this project began, few measurements existed on binary or multicomponent gas-ice systems at pressures of the order of 1 GPa. We set out, therefore, to determine some relevant pressure-temperature-composition (P-T-X) regions of the hydrogen (H_2) - helium (He) - water (H_2O) - ammonia (NH_3) - methane (CH_4) phase diagram. These experiments, and theoretical modeling of the relevant phases, are needed to interpret ice-gas systems of planetary interest.

Our first goal was to show that the data needed to characterize compositions and structures of a multi-phase, multi-component system at very high pressures can be obtained with reasonable precision. We began with water-rich solutions of ammonia for several reasons. These mixtures are relevant to planetary interiors and are relatively easy to prepare. A few parts of the relevant P-T-X space had been determined. These include: the P-T surfaces of pure water [see, for example, Mishima and Endo, 1980] and pure ammonia [Mills et al., 1982] and the T-X surface of ammonia-water at atmospheric pressure [Rollet and Vuillard, 1956] which includes two water-rich compounds ammonia dihydrate ($NH_3 \cdot 2H_2O$) and ammonia hydrate ($NH_3 \cdot H_2O$). The dihydrate is the ammonia-bearing phase most likely to occur near the surfaces of icy planets. Recent models [Lunine and Stevenson, personal communication] suggest that both dihydrate and hydrate are important in the evolution of the interior and surfaces of the icy satellites. The work was begun by Ms. Andrea Koumvakalis and Dr. Mary Johnson [Johnson et al., 1985] and is being continued by Mr. Steven Boone and Mr. Hyunchee Cynn.

Even for this relatively simple system, many experimental problems had to be overcome. The structures of some of the solids are very different from the structure of the liquid. These solids are difficult to grow, and liquid or a glassy solid often persists metastably at conditions where crystals should form. Ice VI and ammonia dihydrate are very troublesome. Despite many attempts to overcome this metastability, it is not clear that equilibrium boundaries have been established among these phases and the liquid. All of the phases also are colorless; and the structures and vibrational spectra of many of the phases are not known. Thus, we learned to identify phases by shapes and birefringence. These observations do not identify phases unambiguously; however, they help us to determine how to grow authentic samples of pure phases.

A manuscript submitted to the *Journal of Geophysical Research* during August 1986 describes Dr. Johnson's studies of the phase diagram of

$(\text{NH}_3)_x(\text{H}_2\text{O})_{1-x}$ at pressures to 5 GPa, temperatures from 240 to 370 K, and ammonia compositions to 50%. Particularly careful studies were made near 5, 10, 15, 20, 25, 30, and 34% in an effort to resolve questions about metastability of the liquid and possible differences between visual work in the diamond-cell and thermophysical measurements in a large piston-cylinder apparatus. Dr. Johnson showed that melting at 20% NH_3 and higher compositions is complex; the composition of the high-temperature solid phase varies with both temperature and time; and the phase diagram can be reasonably well constrained by these data. Other results obtained from Dr. Johnson's work are:

1. At 25° C and lower temperatures, five well characterized and well behaved phases were observed, including: liquid; ice VI; ice VII; an ammonia hydrate; and an ammonia dihydrate.
2. At 3.45 GPa, dihydrate reconstitutes into myrmekitic intergrowths of Ice VII with a higher-relief phase which seems to be isotropic. The high-pressure phase was shown to have a composition near $\text{NH}_3 \cdot \text{H}_2\text{O}$. The transition is either independent of temperature or has a negative P-T slope. Hydrate plus Ice VII remains stable at room temperature to 14.7 GPa. Whether the low-temperature and high-pressure hydrates are equivalent must still be examined.
3. To the limits of precision of this study, none of the boundaries between solid phases of water ice are shifted by the presence of ammonia, although melting is suppressed in the expected manner.
4. At room temperature, the Ice VI-dihydrate-liquid eutectic is at 17 atom percent ammonia and 1.58 GPa. The eutectic curve as a whole may be fit by the equations: $T = 174 + 1.125 P - 0.0229 P^2$ ($r = 0.83$) and $X = 13.35 + 0.0252 P$ ($r = 0.96$). 5. The dihydrate-liquid field has an unusually-shaped region of stability. Dihydrate becomes very prominent in the high pressure regime. At room temperature, dihydrate melts at 0.88 GPa.

Mr. Steven Boone is extending the visual studies system in the diamond-anvil high pressure cells, especially near 33% NH_3 .

Mr. Hyunchee Cynn used the data obtained by Dr. Johnson to grow single crystals of ammonia dihydrate at room temperature and has begun to determine their structures by x-ray diffraction. Preliminary data suggest that dihydrate has a monoclinic-B structure. The lattice constants were: $a = 709.80$ pm, $b = 568.86$ pm, $c = 886.64$ pm, $\alpha = 90.008^\circ$, $\beta = 109.545^\circ$, and $\gamma = 90.401^\circ$. While the diffraction work continues, Mr. Cynn also has grown single crystals of dihydrate for Raman and infrared spectroscopy.

Drs. Johnson and Nicol are involved in two other projects of planetary interest. (1) Chemical reactions during shock compression of simple molecules are being followed by spectroscopy in order to evaluate how the reactions affect the interpretation of equation of state data obtained by shock methods. (2) Temperature and x-ray diffraction measurements are being

made on resistively heating wires in diamond-anvil cells in order to obtain phase and structural data relevant to interiors of terrestrial planets.

Shock compression data are the other major source of equations of state for H-C-N-O compounds at pressures and temperatures inside planets. However, many compounds undergo chemical reactions during shock compression. The products and kinetics of these reactions are not understood, and the effects of the reactions have not been fully considered in reducing shock wave data to equations of state. With benzene as a prototype, we use molecular emission spectra to detect products of these shock reactions at pressures between 20 and 65 GPa and temperatures between 2000 and 5000 K.[Johnson et al., 1986] The spectra show many bands of C₂ and other small molecules. Recent experiments with doubly-shocked material suggest that kinetics of the post-shock reactions can be followed.

Another shock wave project involves a "synthetic Uranus", a solution of iso-propanol, ammonia, and water with C:N:O compositions of cosmic abundance. In addition to the spectroscopy, shock equations of state and electrical conductivities of this "planet" are being measured. Other starting mixtures also will be studied in order to determine whether the results depend strongly upon the initial chemical species.

Drs. Boehler, Johnson, and Nicol also developed techniques for measuring the temperatures of resistively-heated iron and other metals in gasketed diamond-anvil cells.[Boehler et al., 1986] Dr. Boehler has applied these techniques to determination of the phase diagram of iron and, with collaborators from Paris VI, Paris-Nord, Riso, and HASYLAB, they are obtaining high-pressure, high-temperature x-ray diffraction data for alpha, gamma, and epsilon iron that are needed to understand the nature of the Earth's core.

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